The Separation of SEC Curves of HDPE into Flory Distributions

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SYNOPSIS

A technique is reported here whereby molecular weight distribution curves from size exclusion chromatography (SEC) obtained on high-density polyethylene (HDPE) can be deconvolved into a series of Flory-distribution curves using a commercially available computer software system. Our analysis has shown that five to seven individual Flory distributions describe HDPE with better than a 99.9% degree of fit. We impute from this that, upon taking proper precautions, we can consider these HDPE resins to be derived from at least this number of distinct catalyst sites and, furthermore, that modification of the sites will lead to a modification of the resultant resin. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

As can be seen in any standard polymer textbook, Flory-distribution functions represent the "most probable distribution" to be obtained from random polymerization processes using homogeneous catalysis.[1,2] They have the property that $M_n : M_w : M_z = 1 : 2 : 3$. This is not, however, the distribution observed in commercial high-density polyethylene (HDPE).

The breadth of the molecular weight distribution in the case of heterogeneous catalysis, such as for polyolefins, was noted by Natta.[3] He opined that since the molecular weight distributions (MWDs) of heterogeneous-catalyzed polymers are broader than Flory distributions, there must be multiple catalyst sites, each being characterized by a different site geometry. Each site produces HDPE characterized by a distinct Flory distribution with its own number-average molecular weight (M_n). Contributions from the various sites result in the polydisperse, non-Flory distribution $(M_w/M_n > 2)$ product observed.

Pegoraro,[4] assuming that there were many kinds of active sites, used Flory distributions to model the broad MWDs of polyolefins. This work was before

size exclusion chromatography (SEC) was developed, so no quantitative work was done. This concept was subsequently developed into a model by Gordon and Roe[5] to show that the broad distributions could result from catalyst surface effects in heterogeneous polymerizations leading to the observed MWD of Ziegler and Phillips-catalyzed polymers. Clark and Bailey[6] attributed the MWD of such polymers to nonuniform catalyst surface sites.

Cozewith and Ver Strate[7] showed that as a Ziegler catalyst system is driven from solubility to insolubility by changing the catalyst composition it changes from a single-site to a multisite system. This results in a broadening of the polymer MWD from the Flory distribution produced by the soluble catalyst. This work was expanded by Doi et al.,[8,9] who made polymerizations over a range of temperatures where the catalyst went from soluble to insoluble (homogeneous to heterogeneous). They also found that the soluble catalyst produces a Flory distribution polymer and that the insoluble catalyst produces one that is much broader. They attributed this to the presence of multiple sites. They further explained this by pointing out that HDPE is prepared using heterogeneous (insoluble) catalysts.

The influence of a finite number of types of active sites on the MWD has been discussed by Böhm.[10] In addition, Rishina and Vizen[11] and Vizen and Yakobson[12] have provided very convincing evidence that site heterogeneity is responsible for MWD

broadening. These investigators showed there are at least two types of sites on early Ziegler–Natta catalysts including Stauffer AA TiCl$_3$–triethylaluminum. They further showed, using Laplace transforms from the polymerization mechanism equations for the TiCl$_3$–triethylaluminum chloride system, that at least four types of sites are required to make the calculated MWD curves resemble the GPC curves. Courtine[13] examined the crystal structure of Ziegler–Natta catalysts, finding multiple sites. He calculated how they would effect the MWD.

Caunt,[14] in an elegant set of experiments, examined the kinetics of Ziegler–Natta polymerizations and found the catalysts to have a "spectrum of active sites." In addition, Chee[15] also attempted to model the MWD of polymers from kinetics and multisite hypothesis considerations. Nielsen's examinations of the crystal structures of unsupported catalysts suggest that various distinctly different types of catalyst sites do exist.[16]

Floyd et al.[17] showed that broad MWDs can occur without invoking diffusion effects provided that multiple catalyst sites are active. They have modeled these systems to show how multiple sites lead to broad distributions. McLaughlin and Hoeve[18] reported that they were able to separate both a laboratory-prepared polypropylene and a Ziegler–Natta-catalyzed HDPE, with M_w/M_n = 8.6, into Schultz–Flory distributions, each of which was attributed to a "reactive site." Finally, Rebensdorf[19] demonstrated the existence of two or three different Cr(II) or Cr(III) species present in an activated Phillips catalyst for HDPE production. These are shown to have differing reactivities.

The concept that the total MWD of a polyolefin is caused by superimposing individual Flory distributions from multisite centers has further been discussed in reviews by Zucchini and Checchin[20] and by Kissin.[21]

The literature shows that polymer chemists have attempted to determine if the MWD obtained can be expressed as a combination of Flory distributions. The function used to describe the Flory distribution is of the form

$$Y = X(M/M_n)^2 e^{(-M/M_n)}$$

where Y is the concentration by weight corresponding to molecular species M and M_n is the number-average molecular weight associated with the distribution. Since the function is a Flory distribution, the weight-average molecular weight $M_w = 2M_n$, and the "Z" average molecular weight M_z, = $3M_n$. X is a proportionality constant. Y can be shown to be

proportional to $dC(M)/d \ln M$, the change in concentration with log-molecular weight. This differential is what the SEC chromatograph shows.

Smith[22] did a mathematical analysis of SEC data in an attempt to show how one can represent an actual SEC chromatograph as the sum of a series of mathematical distribution functions. However, his distribution functions were not polymerization-based (Flory-type) distributions. Similarly, Fishman et al.[23] deconvolved chromatograms of tomato pectin into Gaussian distributions to prove that these pectins are derived from a mixture of five molecular species.

Broyer and Abbott[24] attempted deconvolution of MWD curves into several component distributions, including Flory distributions, but the program developed was not user friendly enough to be of everyday utility to the catalyst chemist.

Peakfit® is a commercial software system marketed by Jandel Scientific, Corte Madera, CA. It has some 29 canned functions that can be used to deconvolve analytical curves into a maximum of eight predefined mathematical functions that are not necessarily of the same form. It will also permit the user to define one or two functions that can be used alone or in combination with the functions provided to permit deconvolution. For our work, none of the canned functions was found to be desirable. We were able, however, to develop our own function that was able to deconvolve SEC curves.

Function

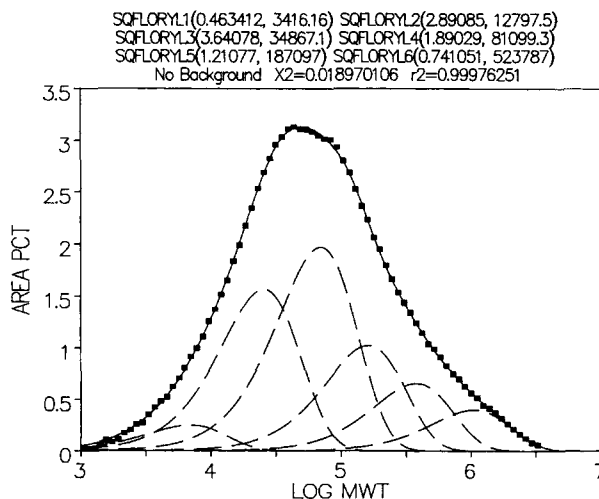The function we have defined as the Flory distribution for use by Peakfit is

Figure 1 Deconvolution of the MWD of an HDPE resin.

Table I   Analysis of Deconvolution of HDPE Resin

	Peak Analysis		Moment Analysis			
Peak No.	Weight Fraction (%)	M_n	Molecular Weight	M_n	M_w	M_z
1	4.28	3416.2	GPC reconstituted	25687	172497	829817
2	26.68	12797.5		21798	172279	845297
3	33.60	34867.1				
4	17.44	81099.3				
5	11.17	187097.0				
6	6.84	523787.0				

Degree of fit: 99.98%.

$$Y = A_0(X/A_1)^2 e^{(-X/A1)}$$

In this relationship, Y is the percent by weight of resin having molecular weight X.

We have cast this into a form in which the molecular weight is plotted in the traditional logarithmic fashion. We devised a Lotus 1-2-3® program to show that this function does, in fact, generate a Flory distribution, i.e., $M_n : M_w : M_z = 1 : 2 : 3$. A typical deconvolution of an HDPE resin is shown in Figure 1 and Table I.

We have found, further, that HDPE resins produced using a standard Phillips catalyst, but differing by melt index, produce deconvolved curves with essentially the same molecular weights but differing concentrations. This is shown in Table II.

In additional work, using comonomers, a series of resins with varying densities and MWDs was produced. All the resins fell within this pattern. By contrast, resins prepared with different catalyst systems have different sets of Flory distributions. Our deconvolution studies of Phillips-type HDPE systems show that there must be at least five dif-

ferent kinds of virtual sites producing Flory molecular weight distributions. A later paper will detail the kinetics of a Ziegler–Natta system to delineate the kinetics and the nature of the sites required to produce its polymer.[25]

CONCLUSION

As can be seen from the literature, our goals have long been sought by the catalyst chemist and modeler. Further, we do wish to state that one must be cautious in drawing final conclusions about the number of catalyst sites from the deconvolution alone. There are obviously many sources of MWD broadening, such as temperature change, mass transfer condition, or multireactor technology wherein the propagation, transfer, and other polymerization constants are functions of time and/or molecular weight. In these cases, deconvolution without background information will be misleading. However, our studies show that used with appropriate additional information, deconvolution is a powerful tool that aids in the understanding of polyolefin catalysis.

Basically, our contribution is twofold: (1) to show that anyone with a PC can deconvolve MWD data to guide his/her research, making this tool available to everyone and (2) to show that we have deconvolved SEC data of HDPE into Flory distributions in an attempt to define the number of implicit polymerization sites necessary to produce these resins.

Table II   Effect of MI on Deconvolution of HDPE

	Resin A[a]		Resin B[b]	
Site No.	Wt %	M_n	Wt %	M_n
1	4.00	2946	3.38	2429
2	26.37	13038	21.10	12743
3	38.96	39972	38.39	41321
4	21.01	122835	24.11	127056
5	9.66	456981	14.03	469590

[a] M_n 25,600; M_w 170,000; M_z 800,000.
[b] M_n 31,000; M_w 272,000; M_z 824,000.

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